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12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release Distribution in unclassified		13. ABSTRACT (Maximum 200 words) We have developed a new synthesis of aldehyde precursors to second and third-order nonlinear optical materials. In this procedure, aldehydes with extended conjugation can be conveniently prepared in one step from organolithium reagents and vinylogous amides. We have also synthesized some donor-acceptor substituted thiophenevinylene oligomers that display enhanced optical nonlinearities and that have been incorporated into poled polymer. Although the compounds had large nonlinearities, insolubility precluded incorporating large amounts of the compounds into the host-guest polymer systems. Finally we have synthesized a series of compounds that have allowed us to map out the behavior of the first hyperpolarizability as a function of ground-state polarization and bond length alternation. The ground-state polarization was monitored by infrared spectroscopy using the local vibrational modes of a functional group on the end of the molecule as a probe.	
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1. ANNUAL TECHNICAL REPORT

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a) A comprehensive list of objectives of the research effort.

The primary objectives of this work are train undergraduate students to perform chemical research and motivate them to enter graduate school in chemistry. Additionally, we seek to develop a variety of molecules whose second-order nonlinearities have been optimized, develop techniques to efficiently synthesize these molecules, and develop second-order molecules that can be covalently attached to polymers. Finally phthalocyanine molecules for optical switching will be developed.

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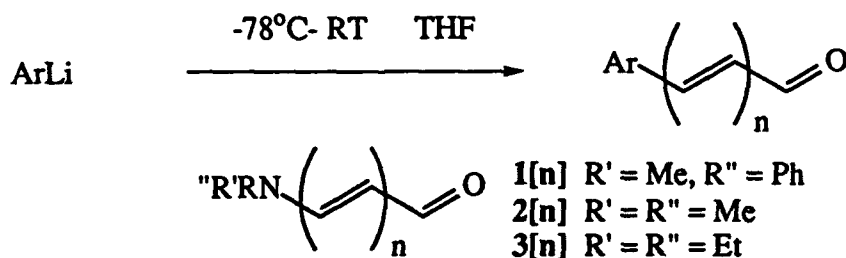


b) Status of the research effort

Convenient syntheses of aldehyde precursors for nonlinear optics --Ed Yang

Often, the key carbon-carbon bond forming steps in the syntheses of nonlinear optical materials necessitate a variety of polyene aldehyde precursors. Current approaches to polyenal compounds include extensions of shorter aldehydes by either one or two double bonds. We have found a convenient route to convert aromatic halide and heteroaromatic compounds to aromatic polyenals with up to three ethylene repeat units in a reasonably general one-pot process. The procedure was then used to synthesize a variety of precursor aldehydes in order to explore the nonlinear optical properties of variable-length donor-acceptor polyenes.

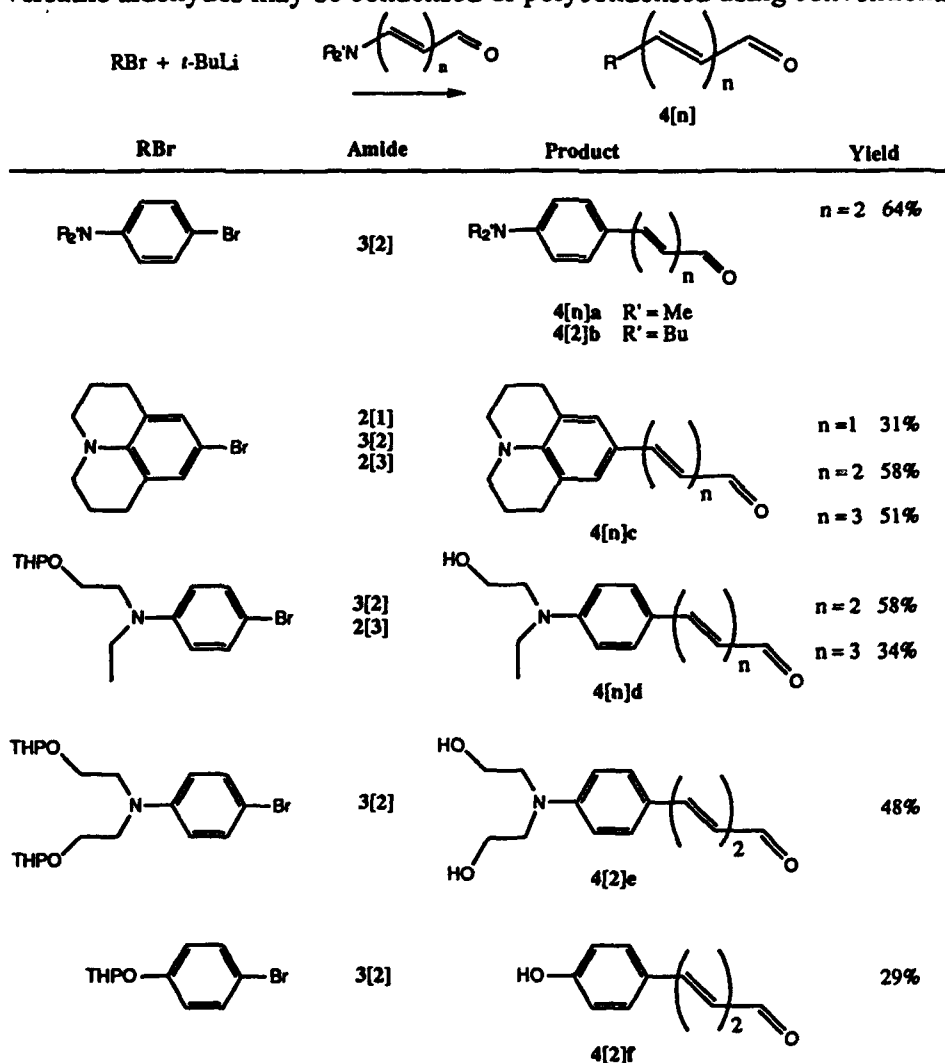
The key sequence in the general reaction scheme below is reminiscent of the synthetic method of Jutz, using which Grignard reagents were treated with N-methyl, N-phenylpropen-1-al (1[1]) or its higher vinylog, 1[2] in yields of 5-95%. In our procedure we use a wide variety of organolithium reagents available from lithium-halogen exchange of t-butyllithium with aryl bromides or heteroaromatic compounds. The bromides were available from a facile high yield procedure for bromination of julolidine or commercial. Here we demonstrate that organolithium reagents add to known ω -N,N-dialkylaminopolyenals 2[n] and 3[n] ($n=1-3$) to make substituted polyenals or polyene-dialdehydes. The method provides a one-pot synthesis of short ($n=2,3$) polyenals 4[n] in as much as 64% yield.



Several families of donor-substituted aldehydes were synthesized and characterized. The structures of the reagents and products as well as yields are given in Table 1. It is especially useful to make comparisons of reactivity and yield based on amide lengths and donor identities in the series 4[n]a and 4[n]c. Polyenals containing the commonly-utilized donor group (N,N-dimethylamino)phenyl were obtained in the highest overall yields, probably due to the fact that they are relatively stable under reaction conditions and thus easily isolated in pure form. Interestingly, 4[1]a and 4[1]c were formed in substantially lower yields than 4[n]a and 4[n]c

($n=2$ and 3). This is in contrast to the behavior reported for reactions using amides **1**[n], where yields up to 95% were obtained with $n=1$ and up to 60% with $n=2$.

Results presented here demonstrate that an array of aryl-capped polyenals and polyenedials of various conjugation lengths may be produced using one-pot general synthetic route in satisfactory yield for materials applications. Starting materials are either commercial or synthesized using literature procedures. The method is compatible with protected protic or carbonyl functionalities. Once rapidly produced with the general procedure described here, these versatile aldehydes may be condensed or polycondensed using conventional chemistry.



Ed Yang performed this work following his freshman year at Stanford. He is an exceptionally bright and hard working young man. He continues to do exceptionally well at Stanford and is planning on majoring in chemistry.

Materials with Thiophene Bridges for Second -Order Nonlinear Optical Applications---A. Jennifer Niessink, done in collaboration with Sandra Gilmour of JPL and Alex Jen of EniChem America.

We have found that compounds containing the N,N' diethythiobarbituric acid and 3-phenyl-5-isoxazolone acceptors can have unprecedented nonlinearities. The N,N' diethythiobarbituric acid and 3-phenyl-5-isoxazolone compounds with the largest nonlinearities also contain extended polyene chains, which although they are excellent bridges for charge transport, compromise the high temperature stability of the materials needed poled polymer applications. Jen *et al.* have synthesized and characterized several alkyl amino donor thiophene stilbene compounds with a range of acceptors including nitro, dicyanovinyl and tricyanovinyl. Their results indicate that the thiophene compounds have much greater nonlinearities than the analogous compounds containing phenyl rings. In this work, we seek to determine whether it is possible to simultaneously achieve large nonlinearities excellent thermal stability by adding an extra thiophene to the conjugated chain and by using acceptors which gain aromaticity upon charge -separation. We will present the syntheses and electro-optic coefficients of three compounds.

Experimental

The syntheses of compounds 6, 8 and 9 (Table 1) have been described previously. Scheme 1 illustrates the syntheses of the compounds with three linked thiophene rings, 7 and 10. These compounds were purified by chromatography on silica and recrystallized from dichloromethane by adding hexanes. Characterization was performed by electronic absorption and ^1H NMR spectroscopy, as well as elemental analysis. The $\mu\beta$ values, where μ is the molecular dipole moment, were measured in dioxane solution by electric field induced second harmonic (EFISH) experiment using 1.907 μm fundamental radiation. Non-resonant r_{33} coefficients of poled, 1 μm thick films of a poly(methyl methacrylate) (PMMA) host matrix loaded with 1 or 2 mole % of chromophore were obtained by a thin film ellipsometry technique using a 1.3 μm laser diode source. The films were poled by applying a DC voltage across the film of 100 V while the sample was held above the glass transition temperature at 120°C for two minutes. With the field still applied, the sample was then allowed to cool to room temperature. For guest-host systems the % loading was limited by the solubility of the chromophore in the PMMA/chlorobenzene film-casting solution.

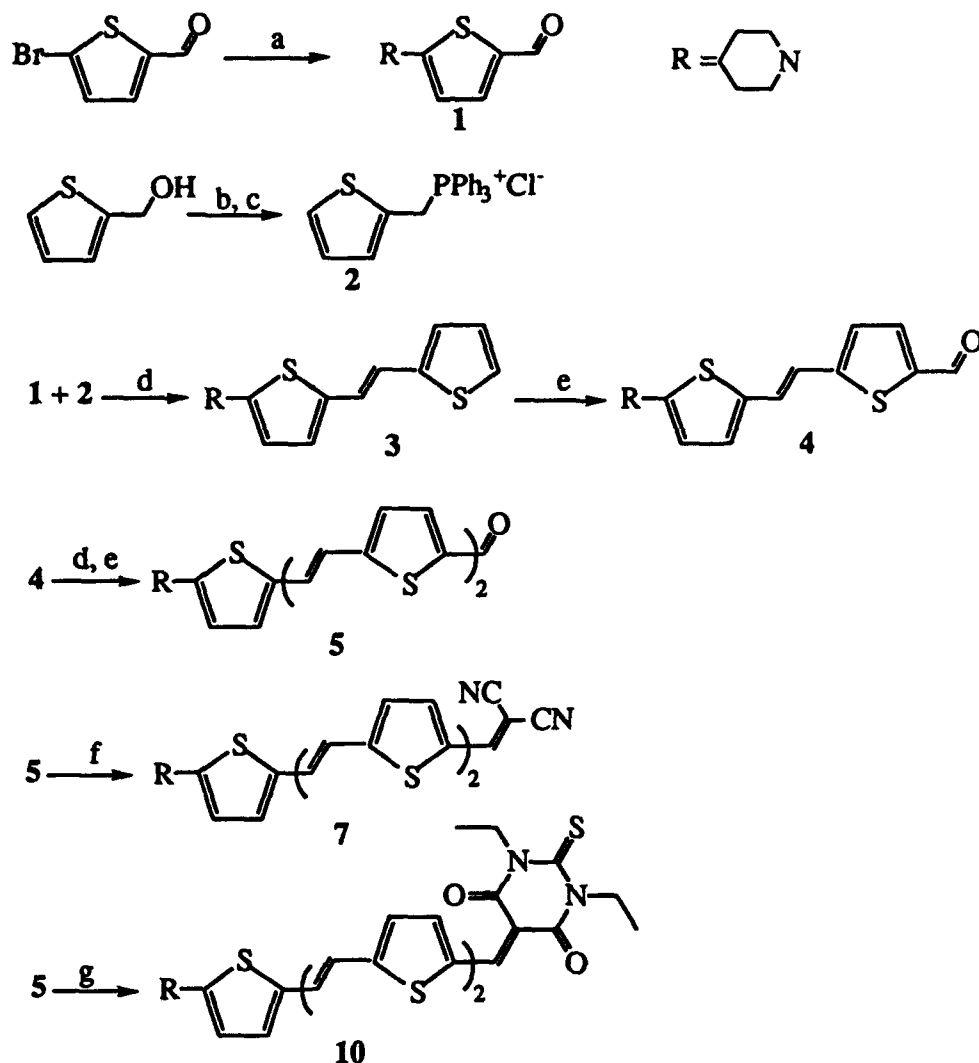
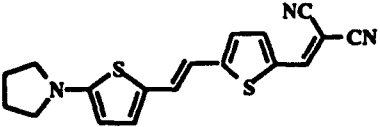
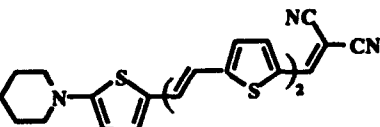
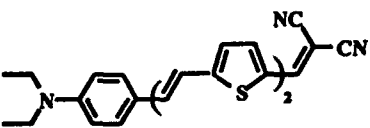
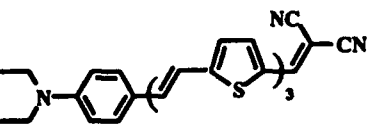
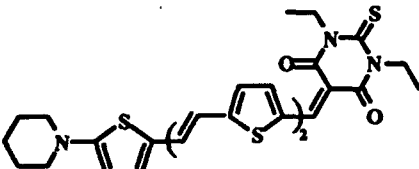


Figure 2: Reactions schemes for the syntheses of thiophene chromophores. Steps: (a) piperidine, dimethyl sulfoxide, aliquat 336, 110 °C, 48 hr. (70%); (b) 37% hydrochloric acid, -10 °C, 1 hr (98%); (c) triphenyl phosphine, ethanol, room temp., 18 hr. (65%); (d) ethanol, sodium ethoxide, argon, 1 hr. (57%) (e) i) n-butyl lithium, dry tetrahydrofuran, argon, -50°C - room temp., 1 hr. ii) dimethyl formamide, -70 °C, argon, 5 min. iii) 10% hydrochloric acid (70%); (f) malononitrile, triethylamine, chloroform, 65 °C, 30 min. (63%); (g) N,N' diethylthiobarbituric acid, piperidine, ethanol, 85 °C, 30 min. (30%).

Table 1. Optical absorption maxima (λ_{\max}) in dioxane, the scalar product of μ and β , $\mu\beta$, as determined by EFISH, the zero frequency form of $\mu\beta$, ($\mu\beta(0)$) corrected for dispersion using a two-state model [16], and r_{33} normalized to 2 mole % loading for thiophene containing compounds.

	Compound	λ_{\max} (nm)	$\mu\beta/10^{-48}$ (esu)	$\mu\beta(0)/10^{-48}$ (esu)	loading (mol%)	r_{33} (pmV ⁻¹)
6		584	2680	1520	2.0 [†]	2.7 [†]
7		566	4450	2630	1.0	2.2
8		547	2370	1460	-	-
9		556	3910	2360	-	-
10		608	5220	2780	1.0	3.4

[†]The chromophores in the electro-optic polymers have piperidine rather than pyrrolidine donors

Discussion

As can be seen from Table 1, large nonlinearities as compared to molecules such as 4-N,N'-dimethylaminonitrostilbene (DANS) ($\mu\beta = 480 \times 10^{-48}$ esu) are observed for the thiophene containing chromophores. Introduction of a phenyl group is clearly seen to decrease the nonlinearities. Compound 7 which is analogous to compound 8 except that one thiophene has replaced a phenyl ring possesses a $\mu\beta(0)$ of around two times greater than that of 8. In fact, even compound 9, with an extra phenyl ring preceding the three thiophene rings, (and is thus

three double bonds longer than 7), still has a smaller $\mu\beta(0)$. As the nonlinearity of 9 is almost twice that of the shorter compound 8, it appears that increasing the length of the conjugated chain has not lead to saturation of the $\mu\beta(0)$ value. On comparing compounds 6 and 7 there is a significant increase (1.7 times) in $\mu\beta(0)$ when the extra thiophene ring is added. However, for reasons that are unclear at this time, the enhanced $\mu\beta(0)$ does not manifest itself in an enhanced electrooptic coefficient. As expected, the nonlinearity of compound 10 which contains a thiobarbituric acceptor moiety that gains aromaticity upon charge-separation has the largest $\mu\beta(0)$. This large nonlinearity also manifests itself in the electro-optic coefficient. If one scales the r_{33} to account for the mole % loading, as indicated in Table 1, compound 10 has clearly the largest r_{33} .

One problem associated with the longer, more nonlinear compounds is their poor solubility for use in guest-host systems. For instance, the compounds with three conjugated thiophene rings, 7 and 10, have much lower solubility than the shorter compound 6 and this is restrictive to achieving high loadings of chromophore in a poled polymer film. This in turn limits the magnitude of r_{33} that can be obtained by the guest-host approach. We are presently working on designing compounds which have large nonlinearities, are thermally stable and can be covalently attached to the backbone of various polymers.

Jen Niessink is a very responsible hard working women. Her progress has been quite satisfactory. I believe that her weak point as a scientist is her communication skill. As part of her involvement in this program i she has had to write reports and given oral presentations. The expended in the and the experience she has obtained has been very valuable to her. She will continue to in my group in 1994.

Study of Bondlength alternation in Polymethine dyes--Matthew Perry.

We have been exploring the hypothesis that bond length alternation (BLA) in organic molecules can be correlated with molecular hyperpolarizabilities. In this study, we synthesized the molecules shown in Figure 1. Non-resonant, solvent-dependent, electric field induced second harmonic generation (EFISH) measurements were performed to probe the variation in the second-order nonlinearity as a function of ground-state polarization. The resulting trends, which are fully consistent with our previous theoretical predictions, identified chromophores possessing optimized positive *and* negative hyperpolarizabilities. In this study we monitored the C=O stretching frequencies in the thiobarbituric acid and barbituric acid derivatives by infrared to see whether this parameter could be used as a local measure of charge transfer and BLA. Our preliminary results are quite encouraging. In general, we found that the C=O stretching frequency decreases with increasing ground state polarization. This is indicative of the charge separated resonance form of the molecule contributing more to the ground-state structure and accordingly the bond of interest having greater C-O⁻ character. We are currently attempting to perform a more analytical analysis of the data such that the actual mixing coefficients of the neutral and charge-separated forms of the molecule can be deduced.

Matthew Perry is an exceptionally bright young man. Literally, the day he joined my group, I presented him with data to analyze. He immediately found errors in the data and returned to my office telling me that some had been done incorrectly. I was impressed by the fact that he was both correct and also had the confidence to question our data immediately. At the same time he has a tough skin and accepts criticism well. He is very demanding of himself and actively tries to improve his performance on a daily basis. His progress to date has been excellent.

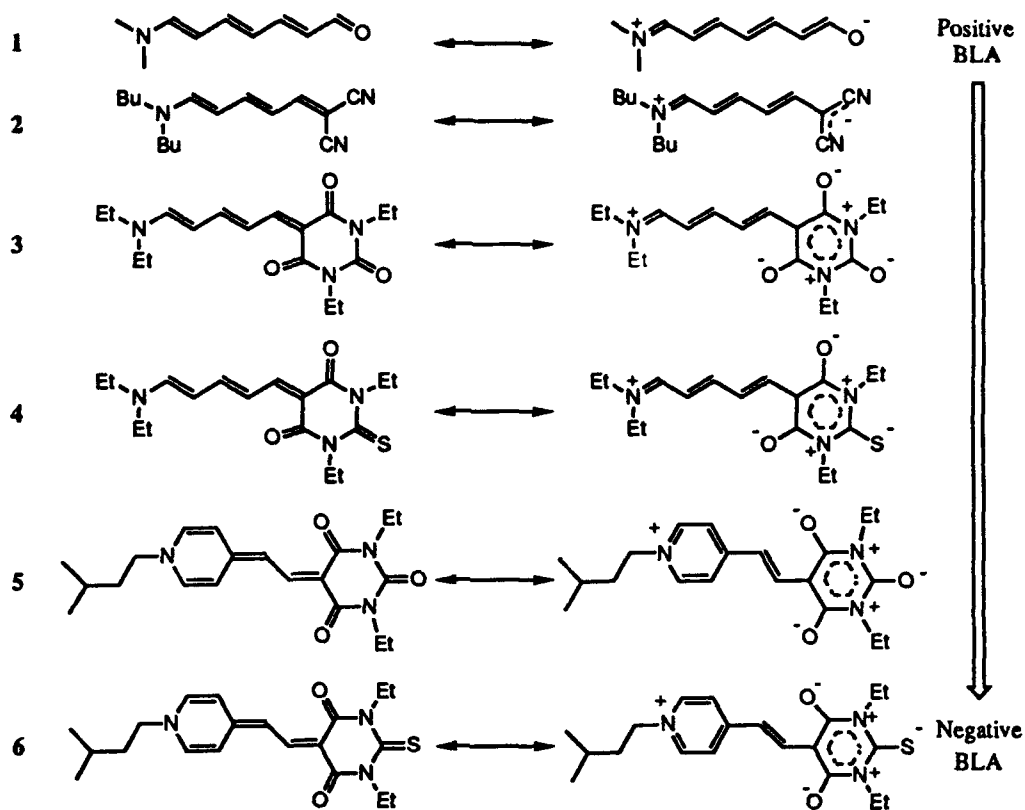


Figure 3. Canonical charge-transfer resonance structures for the donor-acceptor polyenes investigated. Electron donor/acceptor strength in the neutral form increases from 1-6. Et \equiv C₂H₅ and Bu \equiv n-C₄H₉.

c) Cumulative list of publications (With acknowledgment of funds from AASERT award):

1. Mansour, K.; Alvarez, D.; Perry, K.J.; Choong, I.; Marder, S.R.; Perry, J.W. "*Dynamics of Optical Limiting in Heavy-Atom Substituted Phthalocyanines.*" *Proc. SPIE*, **1853**, (1993), 132.
2. Gilmour, S; Jen, A.; Marder, S. R.; Niessink, A. J.; Perry, J. W.; Skindhøj, J.; Cai, M. "*Second-order Nonlinear Optical Properties of Thiophene Containing Chromophores with Extended Conjugation .*" in Materials Research Society Symposium Proceedings Vol. 328, Garito, A. F.; Jen, A.K.-Y.; Lee, Y.-C.; Dalton, L. R. eds, Materials Research Society, Pittsburgh, 1994. p. 485
3. Bourhill, G.; Cheng, L.-T.; Lee, G.; Marder, S. R.; Perry, J. W.; Perry, M. J.; Tiemann, B. G. "*The Relationship Between Second-Order Nonlinear Optical Properties and Ground-State Polarization.*" in Materials Research Society Symposium Proceedings Vol. 328, Garito, A. F.; Jen, A.K.-Y.; Lee, Y.-C.; Dalton, L. R. eds, Materials Research Society, Pittsburgh, 1994. p. 625.
4. Bourhill, G.; Brédas, J.-L.; Cheng, L.-T.; Marder, S. R.; Meyers, F.; Perry, J. W.; Tiemann, B. G. "*Experimental Demonstration of the Dependence of the First Hyperpolarizability of Donor-Acceptor Substituted Polyene on the Ground-State Polarization and Bond Length Alternation.*" *J. Am. Chem. Soc.*, **116**, 2619 (1994).
5. Perry, J.W.; Mansour, K.; Marder, S.R.; Alvarez, Jr., D.; Perry, K.J.; Choong, I. "*Enhanced Reverse Saturable Absorption and Optical Limiting in Heavy-Atom Substituted Phthalocyanines.*" *Optics Letters*, **19**, 625 (1994).
65. Marder S.R.; Cheng, L.-T.; Tiemann, B.G.; Friedli, A.C.; Yang, E. "*Large First Hyperpolarizabilities in Push-Pull Polyenes with Strong Acceptors.*" *Nonlinear Optics*, accepted for publication.

d. Undergraduates who were supported either directly by salary or support for laboratory expenses were:

Matthew Perry

Ed Yang

A Jennifer Niessink

e. Interactions:

i) Papers presented at scientific conferences:

1. Mansour, K.; Alvarez, D.; Perry, K.J.; Choong, I.; Marder, S.R.; Perry, J.W. "*Dynamics of Optical Limiting in Heavy-Atom Substituted Phthalocyanines.*" Presented at Organic and Biological Optoelectronics: Electro-Optics and Lasers Applications in Science and Engineering 93. Los Angeles, CA, January 16-23, 1993.
2. Mansour, K.; Alvarez, Jr., D.; Choong, I.; Perry, K.J.; Marder, S.R.; Perry, J.W. "*Nonlinear Absorption in Metallophthalocyanines.*" Presented at CLEO/QELS. Baltimore, MD, May 2-7, 1993.
3. Cheng, L.-T. Friedli, A.C.; Gilmour, S.; Gorman, C. B.; Marder, S. R.; Perry, J.W.; Perry, K. J.; Skindhøj, J.; Tiemann, B. G., Yang, E. "*The Effect of Bond Length Alternation on The Molecular Hyperpolarizabilities of Polymethine Dyes*" Presented at, The International Conference on Organic Nonlinear Optics, Val Thorens, (France) January 9-13, 1994.
4. Gilmour, S.; Perry, J.W.; Skindhøj, J.; Marder, S. R.; Niessink, A. J.; Cheng, L.-T. "*Second-Order Nonlinear Optical Properties of Polymers Containing Polyene and Thiophene Based Dyes*" Presented at, OL/ LASE Conference, Los Angeles, CA, January 23-29, 1994.

ii) none

f. none

g. none

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Joan Boggs
STINFO Program Manager